

Fatty Acid Composition and Physicochemical Properties of Malaysian Castor Bean *Ricinus communis* L. Seed Oil

(Komposisi Asid Lemak dan Sifat Fizikokimia Minyak Biji Jarak *Ricinus communis* L. Malaysia)

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ABSTRACT

The crude oil of Malaysian castor bean *Ricinus communis* L. seed was extracted by Soxhlet method using hexane. The physicochemical characteristics of castor bean oil were evaluated. The results showed that Malaysian castor seeds contain a relatively high percentage of total lipids content; 43.3% (per dry weight), high iodine value (84.5 mg/g) and saponification value (182.96 mg/g). The seed oil moisture content, acid value and free fatty acid percentage (% FFA) were 0.2%, 4.88 mg/g and 3.4%, respectively. The unsaturated fatty acids (UFA) content were 97.5% of the total fatty acids composition. Ricinoleic acid comprises over 84% while other fatty acids present were linoleic (7.3%), oleic (5.5%), palmitic (1.3%), stearic (1.2%) and linolenic (0.5%), respectively. Five types of castor bean seed oil triacylglycerols were identified as triricinolein, RRR (84.1%), diricinoleoylstearyl-glycerol, RRS (8.2%), diricinoleoyl-oleoyl-glycerol, RRO (5.6%), diricinoleoyl-linoleoyl-glycerol, RRL (1.2%) and diricinoleoyl-palmitoyl-glycerol, RRP (0.9%) respectively.

Keyword: Physicochemical properties; *Ricinus communis* L; ricinoleic acid; triricinolein

ABSTRAK

Minyak mentah biji *Ricinus communis* L. telah diekstrak menggunakan pelarut heksana melalui kaedah Soxhlet. Sifat-sifat fizikokimia minyak telah dikaji. Minyak biji jarak mempunyai peratusan lemak kasar per berat kering 43.3% dan nilai iodin yang agak tinggi iaitu 84.5 mg/g serta nilai penyabunan, 182.96 mg/g. Kandungan kelembapan sampel, nilai asid serta peratus asid lemak bebas masing-masing 0.2%, 4.88 mg/g, 3.4%. Komposisi asid lemak minyak jarak yang diekstrak ditentukan menggunakan Kromatografi gas (GC). Daripada keseluruhan asid lemak, peratusan asid risinoleik adalah paling tinggi iaitu 84% manakala asid lemak lain yang hadir adalah linoleik (7.3%), oleik (5.5%), palmitik (1.3%), stearik (1.2%) serta linolenik (0.5%). Kandungan asid lemak taktepu keseluruhan dalam minyak adalah 97.5%. Sekurang-kurangnya lima triasilgliserol berbeza telah dikenalpasti iaitu masing-masing tririsinolein, RRR (84.1%), dirisinoleoilstearylgliserol, RRS (8.2%), dirisinoleoiloleoilgliserol, RRO (5.6%), dirisinoleoilinoleoilgliserol, RRL (1.2%) dan dirisinoleoilpalmitoilgliserol, RRP (0.9%).

Kata kunci: asid risinoleik; *Ricinus communis* L; sifat fizikokimia; tririsinolein

INTRODUCTION

Castor bean is cultivated for the seeds which yield viscous, pale yellow non-volatile and non-drying oil. It has been used only for industrial and medicinal purposes (Ogunniyi 2006; Ramos et al 1984). It is widely used as a human laxative-cathartic agent, particularly in cases of certain radiological examinations which require prompt and thorough evacuation of the small intestine (Stubiger et al. 2003; Duke 1983). Its botanical name is *Ricinus communis* L of the family Euphorbiaceae, a plant indigenous to many parts of the world. Castor oil is one of the few naturally occurring glycerides with high purity, since the fatty acid portion is nearly 90% of ricinoleic (Akpan et al. 2006). The oil is not only a naturally-occurring resource, it is also inexpensive and environmentally friendly. Relative to other vegetable oil, it has a good shelf life. However, to

kept the quality of the oil, it cannot be left to freeze while kept in storage.

Castor oil has been used for coating fabrics and other protective coverings, in the manufacture of high-grade lubricants, transparent typewriter and printing inks, in textile dyeing (when converted into sulfonated Castor Oil or Turkey Red Oil), in leather preservation and in the production of 'Rilson', a polyamide nylon-type fiber (Duke 1983; Puthli et al. 2006).

India is the world's largest exporter of castor oil; other major producers being China and Brazil. Ramos et al. (1984) had surveyed 36 castor bean varieties in Brazil for oil and fatty acid composition. A large variability of seed oil percentage was observed, ranging from 39.6% – 59.5%. Whereas Ogunniyi (2006) and Gupta et al. (1951) found out that mechanical pressing will remove about 45%

of the oil present and the remaining oil in the cake can be recovered only by solvent extraction.

Castor oil is rich in very unique hydroxy fatty acid; ricinoleic acid $C_{18}H_{34}O_3$ structurally as *cis*-12-hydroxyoctadeca-9-enoic acid, 18-carbon hydroxylated fatty acid having 1 double bond. The structure is illustrated in Figure 1. Many publications reported that ricinoleic acid is a major components in castor oil; 89.2-94.9% (Gupta et al. 1951), about 70-90% by Foglia et al. (2000), 87-90% (Puthli et al. 2006), over 89% (Ogunniyi 2006) and 90.2% (Conceicao et al. 2007). The characteristics of castor oil from other countries such as Brazil, Nigeria, India, China and Africa had been studied. However, only a few research has been carried out on castor oil of Malaysia. The objective of this present work is to determine the physicochemical properties of crude Malaysia castor oil and its fatty acid as well as triacylglycerols composition.

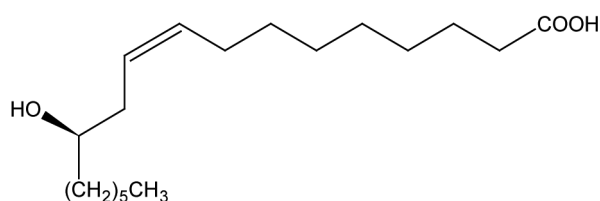


FIGURE 1. Chemical structure for Ricinoleic Acid

MATERIALS AND METHODS

MATERIALS

Castor seeds were collected from various places in Selangor and Kedah. The seeds were dried at 100 - 105°C for 1 hour in an oven to de-hull. The seeds were then selected and the damaged seeds were discarded. Samples were then ground to powder using Waring glass blender prior to extraction.

OIL EXTRACTION

Oil extraction was carried out using Soxhlet extractor. About 5 g of dry ground seeds were first oven-dried at 105°C for 1 hour. The oil was extracted using hexane as solvent. The samples were refluxed for 6 hours in mild temperature (55-60°C) in a Soxhlet extractor. The solvent was then evaporated using rotary evaporator. The extracted oil was kept in an oven at 60°C for 30 min before accurately weighed. The extracted seed oil was kept in a closed container and stored in a refrigerator at 4°C for subsequent physicochemical analysis.

CHEMICAL ANALYSIS

The chemical properties such as iodine value (IV), acid value (AV), free fatty acid (FFA), peroxide value (PV), saponification value (SV) and unsaponifiable matter were determined according to PORIM Test Method (1995) with some modifications. The moisture content was determined using Moisture Analyzer while the water content in the oil

sample was determined using an auto-titration model 701 Karl Fischer Titration Methrom, Swiss.

PHYSICAL ANALYSIS

Viscosity The viscosity of the castor oil was measured using Brookfield Engineering Labs. Inc. Viscometer. The spindle size S05 was used at 100 rpm for 1 min in room temperature.

Refractive Index The refractive index of seed oil was determined using a refractometer Atago Co. Ltd. Series No. 11506, Japan.

Fatty Acid The fatty acid composition of castor oil was determined by Gas Chromatography (Shimadzu GC-17A) equipped with capillary column BPX 70 (30 m × 0.25 m × 0.25 μm) and FID detector. The column temperature was programmed at 120°C with an increment of 3°C per minute for 57 minutes whereas the injector and detector temperature were set at 260°C and 280°C, respectively. Fatty acid methyl ester (FAME) was prepared according to PORIM Official Test Method (1995) with some modifications. The identification of the peaks was performed by comparing the retention times with standard methyl ricinoleate and other individual fatty acid methyl ester.

Triacylglycerol Triacylglycerol (TAG) was determined using High Performance Liquid Chromatography (HPLC). Non-aqueous reverse-phase HPLC separations were performed on a Dionex Ultimate 3000 model with ELSD detector. The mobile phase used was acetone:acetonitrile (63.5:36.5) and the flow rate, column temperature, detector temperature and analysis time were 1mL/min, 30°C, 40°C and 30 minutes respectively. Castor oil samples (2ml containing 0.1ml of oil dissolved in mobile phase solvent), were injected and each TAG peak was identified by comparing with standard TAG based on equivalent carbon number, ECN.

RESULT AND DISCUSSION

PHYSICOCHEMICAL PROPERTIES

The percentage of crude lipids extracted from castor beans and their chemical properties are shown in Table 1. It shows that castor seeds contain a relatively high percentage of total lipids content; 43.3% which is in the same range as reported by Gupta et al. (1951); (35.7%-51.9%) for the African castor oil. Koutroubas et al. (1999) reported that oil content was affected by both locations and castor oil genotypes. The seed oil content depends on the genotype but is also affected by the environmental conditions, cultural practices and time of harvesting. The oil shows quite a high iodine value (IV), 84.5 mg/g due to its high content of unsaturated fatty acids (Table 2). The saponification value was 182.9 mg/g and almost in the same range reported by Ogunniyi (2006) which was 177-182

mg/g. However Ogunniyi discovered that solvent-extracted oil was high in acid value (10 mg/g) compared to the value from the present study which was 4.88 mg/g, respectively. The difference in acid value can be explained due to the quality of the oil and factors such as immature seeds and poor storage condition.

Physically, castor oil is a viscous, pale yellow in colour, clear liquid at room temperature (27°C) and showed no solid fat content at 0°C. The oil is high in viscosity although this is unusual for a natural vegetable oil. This behaviour is due to hydrogen bonding of its hydroxyl groups (Ogunniyi 2006). High percentage of unsaturated fatty acid (ricinoleic acid) keeps it in liquid form even at low temperature.

FATTY ACID COMPOSITION

Table 2 shows the fatty acid composition of castor seed oil. The ricinoleic acid comprises over 84% of the total fatty acid composition. Other fatty acids present were linoleic (7.3%), oleic (5.5%), palmitic (1.3%), stearic (1.2%) and

linolenic (0.5%). The unsaturated fatty acids content was 97.5% of the total fatty acids composition. The ricinoleic acid content from India and Brazil castor bean oils were 94.0% and 90.2% (Gupta et al. 1951) which were higher than Malaysian sample. Low ricinoleic acid content of Malaysian castor bean oil was possibly due to the different in climatic conditions. Fatty acid compositions of samples from Malaysia, Brazil and India were given in Table 2. Even though the samples from Brazil and India contain higher ricinoleic acid, the sample from Malaysia showed almost similar unsaturated fatty acid content which are 97.6%, 98.3% and 97.5%, respectively. This is because sample from India contains no oleic and linolenic acid that make the sample from Malaysia more unsaturated due to the content of polyunsaturated fatty acids (PUFA). However in most cases the castor bean oil consists mainly of 12-hydroxy-9-octadecaenoic acid (ricinoleic acid). Therefore the presence of hydroxyl groups and double bonds makes the castor bean oil suitable for industrial application due to various chemical reactions can be involved.

TAG COMPOSITION

Figure 2 shows the castor bean oil HPLC chromatogram. There are five major triacylglycerol (TAG) peaks and identified as triricinolein (RRR), diricinoleoylstearyl glycerol (RRS), diricino-leoyloleoyl glycerol (RRO), diricinoleoyllinoleoyl glycerol (RRL) and diricinoleoylpalmitoyl-glycerol (RRP). Table 3 indicates that RRR is the highest composition percentage with 84.1%, followed by RRS, RRO, RRL and RRP with 8.2%, 5.6%, 1.2% and 0.9%, respectively. This is the first attempt to report the composition percentage of triacylglycerol contents in castor bean oil using High Performance Liquid Chromatography (HPLC) with ELSD detector.

Ayorinde et al. (1999) used α -cyano-4-hydroxycinnamic acid as a matrix in an acetonitrile/ tetrahydrofuran solvent system, to obtain the matrix - assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectra of castor bean oil. The resulting spectrum showed the same

TABLE 1. Characteristics of Malaysian castor seed oil

Parameters	Value
Lipid content (%)	43.3
Moisture content (%)	0.2
Iodine value (mg/g)	84.5
Acid value (mg/g)	4.9
% free fatty acid	3.4
Peroxide value (meq/kg)	10.2
Saponification value (mg/g)	182.9
Unsaponifiable matter	3.4
Viscosity (cP)	332
Refractive Index at 25°C	1.47
Average molecular weight	937.7

TABLE 2. Fatty acids composition of Malaysian castor seed oil

Fatty acid	Percentage		
	Malaysia	Brazil ^a	India ^b
Palmitic; C _{16:0}	1.3	0.7	-
Stearic; C _{18:0}	1.2	0.9	1.0
Oleic; C _{18:1 ω 9c}	5.5	2.8	-
Linoleic; C _{18:2 ω 6}	7.3	4.4	4.3
Linolenic; C _{18:3 ω 3}	0.5	0.2	-
Ricinoleic; C _{18:1 ω OH}	84.2	90.2	94.0
Saturated fatty acids (SFA)	2.5	1.6	1.0
Unsaturated fatty acids (UFA)	97.5	97.6	98.3

^a Conceicao et al. (2007)

^b Gupta et al. (1952)

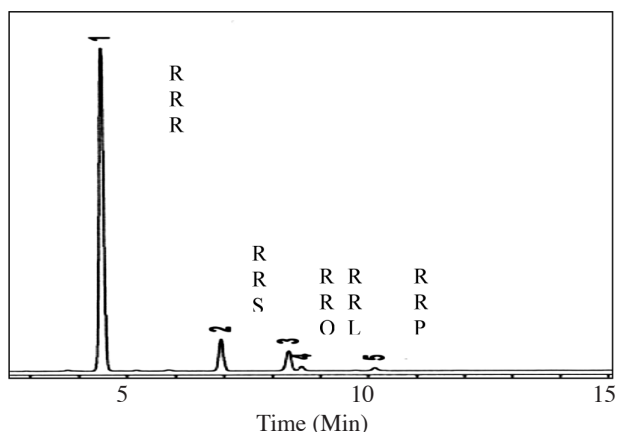


FIGURE 2 . HPLC Chromatogram of Malaysian castor oil

TABLE 3. Major triacylglycerols in Malaysian castor seeds oil

Triacylglycerol	Percentage (%)
Triricinolein (RRR)	84.1
Diricinoleylstearoylglycerol (RRS)	8.2
Diricinoleoyloleoylglycerol (RRO)	5.6
Diricinoleoyllinoleoylglycerol (RRL)	1.2
Diricinoleoylpalmitoylglycerol (RRP)	0.9

occurrence of the 5 major TAG's. Furthermore, Stubiger et al. (2003) obtained a HPLC-UV chromatogram with a considerable number of TAG-related peaks observed within 30 min elution time. It has also been demonstrated that the molecular masses and fatty acid compositions of 8 different castor bean oil TAGs could be determined including arachidic (or dihydroxystearic) acid and gadolic acid; (RRR, RRS, RRO, RRL, RRP, RRLn, RRA, RRG) using either off-line HPLC-positive ion MALDI reflector/TOF/MS with PSD fragment ion analysis or on-line HPLC-negative ion APCI/magnetic sector field MS (Stubiger et al. 2003).

CONCLUSION

In this present work, the fatty acid, triacylglycerols composition and physicochemical properties of Malaysian castor bean oil have been outlined. The Malaysian castor bean oil is very unique with high ricinoleic acid and plausible to recommend for suitable industrial usage. The study revealed that castor seed oil has been proven as a potential local source of ricinoleic acid for further exploration.

ACKNOWLEDGEMENTS

We would like to thanks Universiti Kebangsaan Malaysia (UKM-GUP-NBT-08-27-113; UKM-OUP-NBT-29-150/2010) and Ministry of Science, Technology and Innovation (MOSTI, 05-01-02-SF0199) for funding the project.

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Received: 14 April 2009

Accepted: 10 March 2010